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Electronic Power Research Systems

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*Сирот*

## Types of Alternatives

1. Solvent Wash / Extraction  
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put out  
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2. Detoxification / Decontamination  
Franklin Solvent

3. Landfills.

/ pros - cons

4. Incineration  
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/ expense

5. Feasibility of landfilling on site.

1. Responsibility - ownership. ÷ long term side effects

6. Mobile Incineration

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1. EPA test project.

Charles Rogers

EPA / IERL

Cincinnati Ohio

currently Dixon, Missouri

Pesticide

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EDB -

originals for PCB's

difficulty in Soil Moisture

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references -

papers -

## USE OF FLUOROCARBON 113 IN THE PROCESSING OF LEATHER\*

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### Abstract

Fluorocarbon 113 (FC-113) and FC-113 blends have been investigated as processing fluids in leather manufacture. The technical feasibility of using a fluorocarbon process to produce unhaird, dried, bated, tanned, colored, and fatliquored leather has been demonstrated on a laboratory scale. As an example, raw cowhide or pigskins can be unhaird and dried to give a lightweight, stable product suitable for grading, storage, and shipment. The product can be rehydrated and tanned to give satisfactory quality leather.

Recovery and recyclization of FC-113 is possible because of its high stability, low water solubility, and low latent heat of vaporization. As a result, water pollution problems may be reduced or simplified and energy and water savings realized from the use of this system in leather production.

The paper outlines engineering processes for potential future use by the leather industry.

### Introduction

Two years ago, we reported our work on the rapid drying of leather using FC-113†/methanol drying fluid to economize on energy usage (1). Since that time, we have done considerably more work on drying and other leather manufacturing operations where FC-113 might be advantageously used. This work has

\*Presented at the 75th Annual Meeting of the American Leather Chemists Association, Oconomowoc, WI, June 19, 1979.

†FC-113 is 1,1,1-trichloro-2,2,2-trifluoroethane sold by Du Pont under the trade name, Freon® TF.

led to some revisions and extensions of our previously presented ideas. The technical feasibility and process economics of using FC-113-based systems for a number of leather manufacturing steps have been established. Current assessments are more realistic and, even though some features of fluorocarbon processing of leather are not favorable at present, there are factors which could bring about future changes.

We believe this work to be of general interest to the leather industry, particularly from the viewpoint of the future use of an effective, safe, readily recoverable solvent, as leather technology changes or as environmental restrictions dictate change.

Numerous attempts have been made over the years to replace water as a processing fluid in leather manufacture. Ushakoff (2), some 22 years ago, reviewed nonaqueous systems for leather production and specifically discussed the Secotan process for tanning, fatliquoring, dyeing, and drying, using acetone as the solvent. That process has been used only to a limited extent on a commercial scale, principally because solvent loss is excessive and for reasons of safety. Buechler (3) has also reviewed his work with acetone on a large pilot-plant scale primarily for solvent tanning. Unfortunately, that process was never commercialized for a variety of reasons.

Water has a unique place in process technology because of its availability, low cost, excellent solvency, and low toxicity. In the leather industry particularly, its interaction with proteins via hydrogen bonding is of special importance. On the other hand, some of water's properties can be severe drawbacks. For instance, because of its high latent heat of vaporization and vapor pressure characteristics large amounts of energy must be used to remove it by heat. Also, since water is a solvent for many pollutants, it creates problems which are of vital importance in many industries, and especially in the leather industry.

To quote Poats and Naghski (4), "Pollution of the environment from hide curing and tanning is a serious national and local concern. New Federal standards for industrial waste discharges will require hide processors and tanners to make substantial investments in water treatment facilities if alternative solutions to the problems are not found."

Much of the water in chemical processing is used in excess of actual requirements. The historical precedent for this waste was set when pollution controls were virtually nonexistent and energy costs were much lower. Thus, there is a sound rationale behind attempting to replace at least some of the water used in leather manufacture with fluids which will yield cost savings through energy conservation and pollution abatement, and will at the same time speed up the penetration of leather-treating chemicals without affecting leather quality, or even improving it.

When one considers solvent cost, toxicity, flammability, solvency, hide/solvent compatibility, and recovery, there are not many alternatives to water. One class of compounds exhibiting broad utility because of stability, safety,

moderate cost, and thermodynamic properties are the fluorocarbons, which are widely used as refrigerants, cleaning solvents, and foam blowing agents and in many small-volume specialty applications. But the vastly different solvency of fluorocarbons, especially for salts, does not allow complete replacement of water in all leather manufacture operations. One must think in terms of partial water replacement in unhairing and tanning and full replacement only in processes like fatliquoring and dyeing.

Experimental

In most of our work, a mixture of FC-113 and methanol is used because this combination simulates some of the necessary properties of water and functions as an effective dehydrating agent itself. The FC-113/methanol mixtures exhibit phase behavior (Figure 1) with water which allows facile separation from the water by a combination of gravity (Figure 2) and distillation. The small methanol molecules readily penetrate the matrix of leather fibers to leach out water and are themselves removed with relative ease.

The great diversity of processes for making various types of leather using many kinds of skins and hides for hundreds of applications provides a multitude of opportunities for a potentially new solvent. Conversely, this market poses an equally great number of special technical problems that are difficult for a solvent manufacturer to handle in a general way.

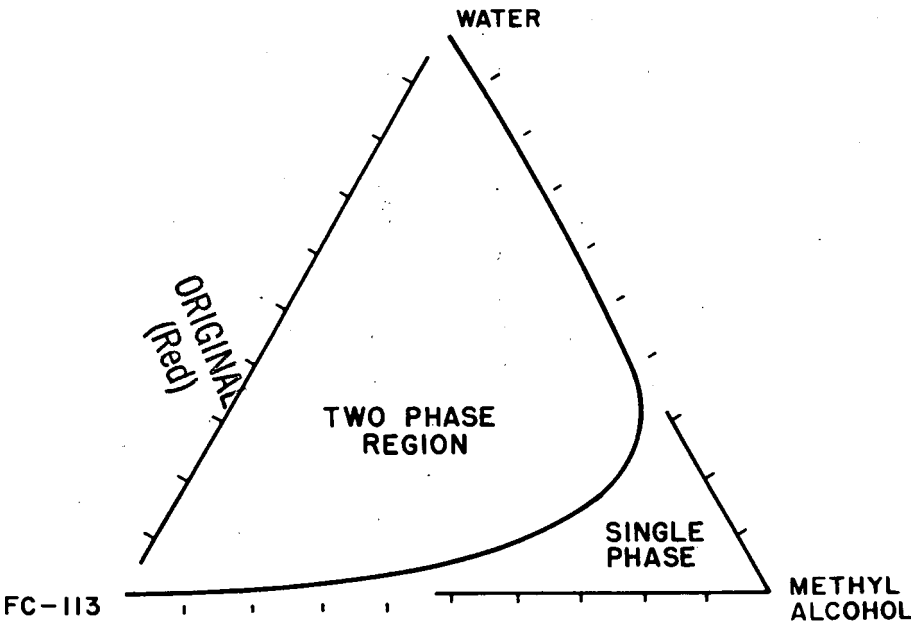


FIGURE 1. -Solubility relationships of FC-113/methanol/water mixtures at 25 C.

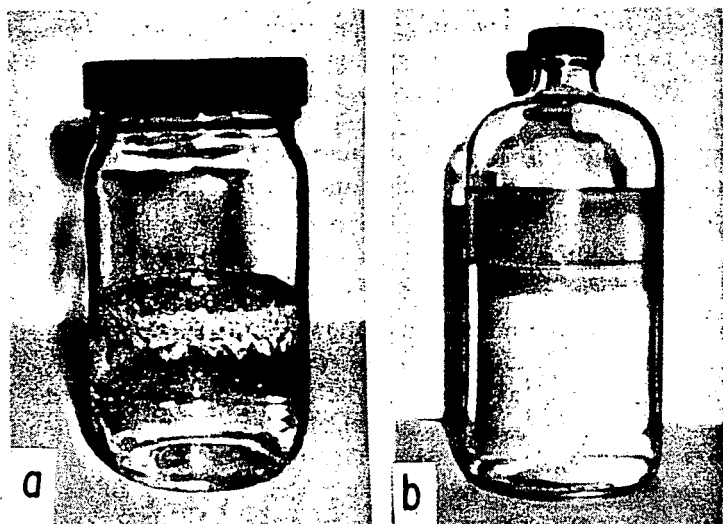


FIGURE 2.—a, Liquid and solids removed during unhairing step showing phase separation; b, typical solvent-based dye bath showing dye chemicals concentrated in aqueous phase.

#### USE IN DYEING

As an example, consider the dyeing of leather, for which we demonstrated the technical feasibility of using a Freon® process with several principal types of dyes. We believe that systems can be developed which would handle a full range of colors with the advantage of significant savings in water and pollution abatement costs, as well as better dye use. However, each dye might have its own specifications for use in the new systems. A dye user might possibly find it practical to develop these specifications, but the cost would be unacceptable for a solvent manufacturer.

#### USE IN UNHAIRING AND DRYING OF HIDES

Clearly, from a business standpoint, we had to demonstrate that there were considerable technical and economic benefits to be derived from the use of fluorocarbon solvents in leathermaking. The principal leathermaking steps we investigated are summarized in Table I. Of these, we chose the earliest steps, unhairing/bating/deliming/drying, as a combination to meet our criteria for the best entry point for a fluorocarbon process. This process could yield a stable dried hide flexible enough for storage and readily rewettable for subsequent operations. Further advantages could include early sorting, shipping weight reduction (less water and no salt), and elimination of chilled storage for the more stable dried hides. Salt-curing would be completely eliminated, thereby markedly reducing pollution problems. Fat and oil recovery would be an added benefit.

TABLE I

USES FOR FC-113 IN LEATHER MANUFACTURING STEPS

| Step                                 | Fluid Mixture   | Efficacy  |
|--------------------------------------|---|---|
| Unhairing                            | FC-113 + water + CaO + Na <sub>2</sub> S + selected enzymes                       | Good hair removal.  |
| Bating, deliming and drying hides    | FC-113 + methanol + NH <sub>4</sub> Cl + enzymes (several varied cycles required) | Hides suitable for long-term storage, rehydration, and tanning. |
| Chrome tanning and vegetable tanning | Conventional tanning chemicals with most of water replaced by FC-113/methanol     | Faster penetration than from water alone.                       |
| Drying tanned stock                  | FC-113/methanol   | Rapid drying. Yields pliable stock.                             |
| Coloring                             | FC-113/water (~10% water)   | Excellent for dyes tested.                                      |
| Fatliquoring                         | FC-113 + fatliquoring agents  | Hides flexible. Solutions easily recycled.                      |

With these objectives in mind, we developed a process, as shown in Figure 3, and a flow sheet (Figure 4), and proceeded to experimentally determine the basic data needed for determining the size and cost of equipment, with the help of our Engineering Department.

Basically, the hide treatment occurs in a series of hide processors, of which only one is indicated schematically in Figure 4. A modified unhairing solution of lime, sodium sulfide, water, and FC-113, together with wet rawhides, is introduced to the hide processor. After 4 to 8 hours of rolling, methanol is added to aid in the separation and filtration of hair sludge. The hair sludge containing water and FC-113 is drained and filtered. The FC-113 phase is passed to a distillation set for recovery of fats, oils, and fluorocarbon. After recovery, the FC-113 is transferred to storage for recycling.

After draining, a methanol/FC-113 mixture (35 wt percent methanol) is pumped into the hide processing unit for a one-hour rolling for the first drying stage. Subsequently, the water/FC-113/methanol is removed, decanted, distilled, and the solvent recycled. A second drying stage, employing fresh FC-113/methanol, follows, after which residual solvents are largely removed using mild heating and vacuum. The final product is a hide of about 35 percent water, which we have shown to be stable for months and which can be tanned satisfactorily after deliming and bating.

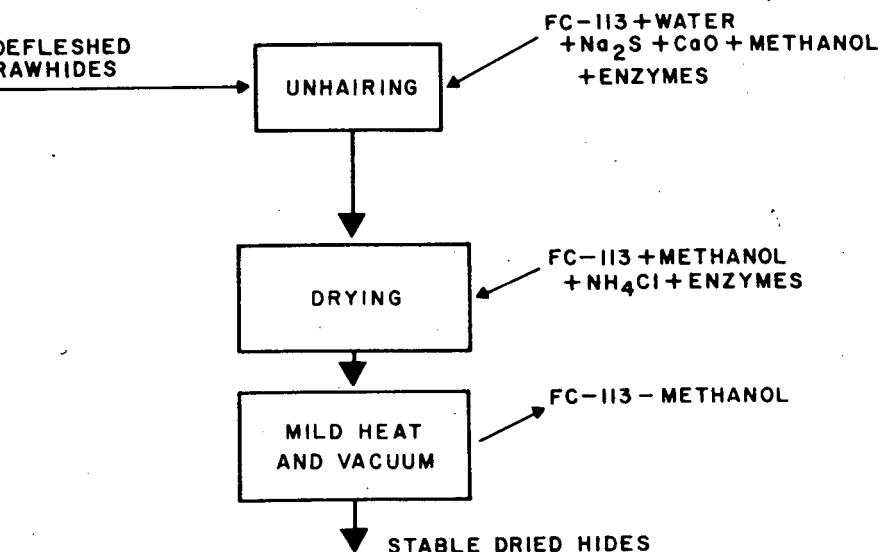


FIGURE 3.—Diagram showing main steps in a fluorocarbon unhairing/drying process for cowhides.

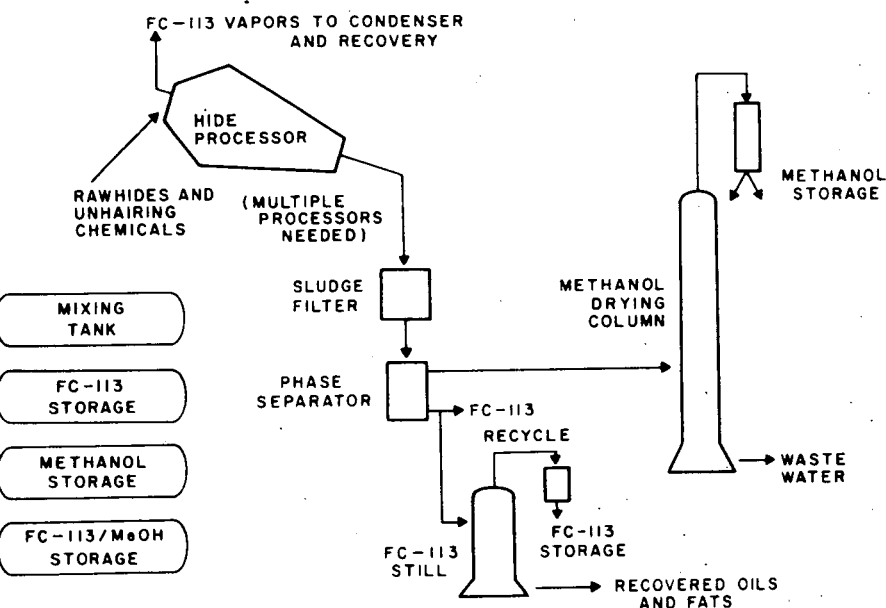


FIGURE 4.—Operation details for a FC-113 solvent unhairing-drying system for rawhides.

#### RECOVERY OF HAIR SLUDGE

A number of specific process features deserve mention. Laboratory tests in miniature filtration apparatus indicated that the hair sludge is filterable at practical rates when methanol is present. This finding may have independent merit inasmuch as hair sludge is generally accepted as being quite difficult to filter. Therefore, the pollution abatement problem with unhairing waste is simpler since no salt is present and the filtered solids can be easily dried and perhaps used as a soil conditioner or fertilizer. The distillation set consists of two columns, the larger being a 20-tray methanol drying column 30 by 5.5 ft. Costing is based on stainless steel for containment of the solvents and chemicals.

Based on bench-scale tests, it appeared that a full cycle for converting green hides to the dried final product would take about 12 hours. To allow a margin of error, our calculations were based on a 24-hour cycle. Discussion with industry people makes us believe that the 24-hour cycle is more realistic, but here, only pilot plant runs would be definitive.

#### COST ESTIMATES

Loss rates for the FC-113 are estimated at about 1 percent, based on the total fluorocarbon throughput. This represents good recovery, and is in accord with our operating experience with other FC-113 uses on smaller size equipment where recovery is somewhat more difficult.

Based on the construction cost index of 249 for the 4th quarter of 1978, we have calculated the estimated investment required to equip a plant for the unhairing and drying of raw cattlehides using FC-113. The estimated major equipment costs (including installation, instrumentation, electrical, and building costs) for a plant to handle 2200 hides a day, running 270 days a year, are as follows:

|                                     |                     |
|-------------------------------------|---------------------|
| 14 hide processors                  | \$ 2,500,000        |
| 2 distillation columns              | 650,000             |
| 1 filter for hair sludge separation | 1,430,000           |
| storage tanks                       | 640,000             |
| miscellaneous equipment             | 1,050,000           |
| allowance for contingencies         | 1,890,000           |
| contractor's fee                    | 3,270,000           |
| <b>total permanent investment</b>   | <b>\$11,430,000</b> |

This total is quite large for new investment in this industry and could not be justified unless more favorable overall economics prevailed for this process.

We have also calculated the operating costs, based on 3 shifts a day, working



the same number of days a year, processing the same number of hides. The costs per day are estimated as follows:

|   |         |
|---|---------|
| labor                                     | \$1,000 |
| raw materials (excluding hides)           | 1,510   |
| utilities                                 | 2,840   |
| indirect costs                            | 800     |
| maintenance                               | 970     |
| plant overhead                            | 1,610   |
| packaging                                 | 350     |
| less credit for recovery of oils and fats | (1,650) |
| net factory cost                          | \$7,430 |

With these operating expenses, the increase in hide value that would be required in order to break even (\$7,430/2200 hides) would be \$3.38 per hide. Since unhaired, dried hide is not currently an item of commerce, it is difficult to estimate what price it might command, so that determining the economic feasibility of such an operation is subject to considerable uncertainty.

In this analysis, we have taken no credit for pollution abatement. The reason is that this figure varies with location and liquid waste discharge regulations, most of which have not as yet been finalized. When the discharge requirements for hide processors and tanneries are known, then a realistic assessment of this subject can be made. A positive assessment would give credit to the greatly reduced and simplified waste disposal characteristics of the fluorocarbon process compared to methods required for handling conventional waste streams. Obviously, pilot-plant operating experience would be required to demonstrate the advantage.

Despite the fact that the required investment for this new technology is large relative to current leather industry standards, we believe that it is worthwhile to keep in mind that an alternative process exists, at least in its early stages, that may help to solve some leather industry problems, especially those concerned with pollution.

**Advantages.** — The advantages of the fluorocarbon process are:

- less water pollution
- easier handling of waste streams
- lower shipping weight
- hides well degreased
- fats and oils from hide readily recovered
- dried hides stable for long-term storage
- hides easily graded
- potential sale of unhairing wastes
- chilled storage of hides not required

These advantages could cause this process to be important in the future, either because of market-place forces or government regulatory action.

Convincing demonstration of the commercial feasibility of the fluorocarbon process requires substantial investment, and it has not been possible to obtain sufficient interest from the leather industry to warrant further process development. Further, federal liquid waste discharge requirements continue to be elusive. Therefore, Du Pont does not see a near-term possibility that the fluorocarbon process can be made attractive to the leather industry and has terminated work on this project. We continue to believe that the concept of using a safe, recoverable solvent in place of water will one day be a reality in leather processing. Meanwhile, we hope the presentation of techniques for the handling of rawhides to quality leather, which have been demonstrated at the laboratory level, will provide the background and stimulus for the future.

## References

1. Bartlett, P. L. and Steinacker, W. R., *JALCA*, 72, 12, 1977.
2. Ushakoff, A. E., *JALCA*, 53, 314, 1958.
3. Buechler, P. R., Address to the American Leather Chemists Association, June 1958.
4. Poats, F. J. and Naghski, J., MTS-191, Nov. 1973.

Received June 19, 1979.

## Discussion

MR. JOHN MOYNIHAN (Discussion Leader): Thank you Warren for your interesting paper. Dr. Thorstensen wants to offer some comments at this time.

DR. THORSTENSEN (Thorstensen Laboratory): Fluorocarbons have some unique features which allow different approaches in leather processing than are possible with other solvents. In its liquid state, fluorocarbon 113 is essentially insoluble in and heavier than water. These properties lead to easy separation by decanting. In addition, fluorocarbon 113 has a very low order of toxicity, a low boiling point, a low heat of vaporization, and is nonflammable. These characteristics allow equipment design configurations for solvent use quite different than those used in the leather industry in the past.

In the unhairing system outlined, the fluorocarbon acts as an inert liquid to cushion the hides under extremely low quantities of water. The high concentration of chemicals in the water phase and the high concentration of sludge in the aqueous layer of the effluent make the discharge of effluent a sludge problem rather than a conventional effluent discharge.

The protein and inorganic portions of the effluent are in the water; the fats are in the solvent. The protein-rich waste sludge can be dehydrated by filtration and drying. The fats are eventually recovered by distillation of the solvent.

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Although chrome tanning can be conducted using the high concentration system and the cushioning effects of the fluorocarbon, it is doubtful that this would be an overall advantage over conventional systems.

With vegetable tanning, faster processing can be obtained. The presence of alcohol in the system is helpful. Recycling of liquors and the recovery of spent solutions could make the system economically attractive. A zero effluent discharge is possible in either vegetable or chrome tanning.

In retanning, coloring, and fatliquoring, we can obtain the advantages of a solvent system in the use of water-insoluble materials. Impregnation, coloring, and leather lubrication with entirely new chemical systems could result in unique leathers.

The dehydration of chrome-tanned blue stock, or crust stock, could result in a lightweight, clean product for shipping. The relationship between solvent dehydration and effects on grain and area might present a serious drawback.

Fluorocarbon processing shows very interesting technical possibilities. The hard questions are whether the advantages and the probability of success can justify the expense of the research. As a part of this project, we visited the technical management of several of the largest and most progressive tanning companies. With the present uncertainties of the leather industry, due to the "hide drain" to the international market, the prospect of participation in a long-range development program held little appeal in spite of the potential benefits. All were interested and wished to encourage Du Pont to continue to pursue the fluorocarbon processing research.

The leather industry has enjoyed strong technical support by its suppliers. The majority of new systems and almost all new chemicals used are the result of research by suppliers in anticipation of sales of proprietary products.

In the case of the fluorocarbon research by Du Pont, it is very evident that further development on a large scale cannot be justified on the basis of anticipated fluorocarbon sales. The economic justification of fluorocarbon process development for the tanner presents an entirely different set of calculations.

It is our hope that publication of the result of this research will stimulate further ideas in the industry.

MR. MOYNIHAN: Thank you, Tom. Do we have any questions from the floor?

DR. PETER BUECHLER (PPG Industries): At what scale was this work finally abandoned? Had you had a pilot plant?

MR. STEINACKER: I don't think we can even call it a pilot plant, Peter, the biggest piece of leather or hide that we processed was about two square feet. We got up to that scale. Most of the work really was done on something closer to ten square inches.

DR. BUECHLER: Thank you very much.

MR. MOYNIHAN: Thank you, Warren, I guess everybody knows all about it by now. (Warren received a certificate of appreciation.)

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## ENERGY REDUCTION THROUGH SOLVENT PROCESSING OF LEATHER

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### INTRODUCTION

Our contribution to energy conservation in the leather industry is not just a modification of existing procedures, but is a more fundamental revision of traditional leather-making techniques involving use of a nonflammable, recoverable solvent. Solvent processing of leather is not a new idea, as I am sure most of you know. There are a number of different schemes that have been tried in the past which use alcohol, or most of the time acetone, to accomplish the solvent processing of leather. However, each time one difficulty or another prevented the operation from being fully accepted and, thus, achieve the degree of acceptance hoped for.

Solvent flammability was one stumbling block, with serious difficulty in mechanical handling of the hides in the presence of the flammable solvent. Another problem was the large quantity of wet solvent that had to be dried and recovered for reuse in order to make the process economical. In this case, we have chosen a completely different solvent that will avoid some of the previous difficulties. Let's start off by reviewing some this solvent's properties before going to the specific operations that have been studied.

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### PROPERTIES OF SOLVENTS

As shown in Table I, the product that we have worked with is 1,1,2-trichloro-1,2,2-trifluoroethane and its blends. This is also known as fluorocarbon 113 or FC-113, which is the name I will refer to from here on. DuPont's trade name is Freon® TF.

One solvent blend that has been used is FC-113 in a constant boiling mixture with methyl alcohol and nitromethane. This is known commercially as Freon® TMS. Both FC-113 and its blend with methanol are nonflammable, so that one of the big problems that has occurred with pure alcohol or acetone in the past is largely avoided. The boiling points are relatively low, just slightly above room temperature for both the products, and they are relatively dense, being about half again greater than water. This, together with the lack of miscibility with water, aids in solvent recovery and recycle through simple gravity water separators.

One of the major advantages of FC-113 is the low latent heat of vaporization, which is only 63 Btu/lb. This compares to over 900 Btu/lb. for water, or only

TABLE I  
SOLVENT PROPERTIES

|  | 1,1,2-trichloro-<br>1,2,2-trifluoroethane<br>(FC-113, Freon® TF) | Constant Boiling Blend of<br>Trichloro-trifluoroethane/<br>Methyl Alcohol/<br>Nitromethane<br>(Freon® TMS) |
|--|--|--|
| Flammable                                  | No   | No   |
| Boiling Point, °F.                         | 117.6  | 103.5  |
| Density, lbs./gal.                         | 13.1   | 12.3   |
| Latent Heat of Vaporization,<br>Btu/lb.    | 63   | 91   |
| Inhalation Toxicity, TLV-TWA<br>ppm by wt. | 1000   | 475  |
| Miscible with Water                        | No   | Slightly   |

1/15 the energy is required to evaporate a pound of FC-113 as compared to water. In our process, this energy reduction is utilized because water is removed as a liquid rather than by evaporation. The low latent heat solvent is all that is evaporated from the leather. This is a tremendous energy reduction and one of the main reasons that leather processing with FC-113 is so important as far as saving energy is concerned.

As far as inhalation toxicity is concerned, the Threshold Limit Value-Time Weighted Average for FC-113 is 1000 ppm. This is the maximum value given any product, except CO<sub>2</sub>, and is the same as for ethyl alcohol and acetone. All of these are far higher than some other nonflammable solvents, such as perchloroethylene which is 100 ppm, and carbon tetrachloride which is only 10 ppm.

In all cases the property values on Table I are slightly different for the blend of FC-113 and methyl alcohol and nitromethane, primarily because of the methyl alcohol content, which is about 6 percent.

Lastly, the FC-113 is not miscible with water. The blend with methyl alcohol is slightly miscible with water, and this will be discussed in more detail later as that's the basis for the drying performance of the material.

APPLICATION

Because of the large energy consumption in conventional drying of leather and the very low latent heat of FC-113, we focused on the drying operation as the first place to establish an economic benefit for solvent processing. It was felt that if drying could be accomplished, then preceding successive steps could be included and still only require solvent removal from leather the one time.

Table II shows how far this has now been extended. Overall, we believe that we've demonstrated that one can start with pickled stock from the beam house

TABLE II  
SOLVENT PROCESSING STEPS

|            |                              |
|------------|------------------------------|
| Beamhouse  | normal operation             |
| Chrome Tan | } FC-113 + Chemicals + Water |
| Retan      |                              |
| Color      |                              |
| Fatliquor  | } Freon® TMS + Chemicals     |
| Dry        |                              |
| Condition  |                              |
| Finishing  | normal operation             |

and process it through chrome tanning, re-tanning, coloring, fat liquoring, drying and conditioning, all in the two solvents mentioned.

To illustrate the principles involved, let's start with pickled stock from the beam house and describe how the chrome tanning operation works. The re-tanning and coloring steps will, in turn, work very much the same way. The pickled stock will be wet with the water content from a wringer and loaded into the equipment with chrome tanning chemicals. A little water is added to allow the chrome tanning chemicals to be distributed throughout the system, and the rest of the fluid volume is then made up with FC-113 and the mixture is agitated until the desired chrome fixation is reached.

One feature of this chrome tanning process is that the chemistry is essentially the same as in conventional use since the reaction takes place in an aqueous medium. However, the chemicals are more concentrated in the smaller dispersed water phase, so that the tanning reaction proceeds more rapidly. There is only enough water to wet the surface and provide for distribution of the chrome, while the continuous liquid phase is FC-113.

The equipment considered for use has been a cement mixer/processor-type or some equipment of that nature that will be tight and hold the solvent well. We don't believe that wooden drums will be satisfactory process vessels because the solvent losses would be too great. The equipment must also provide for ease of draining and refilling, without solvent loss, to allow a number of operations to be done in the same piece of equipment and come out dry, solvent free, and ready for staking.

At the end of the chrome tanning cycle, the fluid is drained off and sent through a simple gravity water separator. The aqueous phase will rise to the surface. It will be separated and returned for reuse with the next load. The essentially pure FC-113 will be drawn from the separator bottom and recycled without purification.

The re-tanning and coloring steps will go much the same way with, of course, different chemicals plus a little water being added each time together with some

agitation and a reaction period. Following this, the solution is drained and the next step taken.

The fat liquoring, drying and conditioning operations will take place during the same cycle. Rather than use pure FC-113, this time Freon® TMS is added to the equipment together with the chemicals required for fat liquoring. Obviously, no water addition is made this time.

Leather drying is made possible by the methanol component of the Freon® TMS. After some agitation, two separate liquid phases form. The top layer contains methanol plus water removed from the leather. This floating layer is easily decanted in a gravity water separator. The water/alcohol layer is sent to a still and the recovered dry alcohol is mixed with FC-113 and thus recycled. This particular operation does represent one flammability problem because of pure methanol distillation. However, the hazard can be kept at a minimum through proper design and good maintenance.

Another potential problem is hide shrinkage. Just how serious this is has not been established and is one of the things that will have to be better defined in the future to see if something needs to be done about it.

The last part of the solvent processing operation is to evaporate solvent from the leather and recover it for recycling. The evaporation, because of the low latent heat and low boiling point mentioned earlier, can go fairly readily since not a great deal of heat is required. This heat can be supplied by jacket steam on the vessel or by recirculating hot solvent vapor to transfer heat to the leather.

At the end of the fat liquoring, drying and conditioning cycle, the water has been removed down to the level at which the hide is ready to be staked, so that no additional conditioning is required. The moisture left in the leather can be varied by the amount of Freon® TMS used for drying to get a 25 percent or 30 percent, or whatever moisture content is desired.

#### ENERGY SAVINGS

Based on these solvent processing steps, there are going to be some energy savings, and Table III shows the magnitude involved. These calculations are

TABLE III  
SOLVENT PROCESSING OF LEATHER

|                                     | Net Energy Savings<br>Btu/Tannery/Yr* |
|-------------------------------------|---------------------------------------|
| Leather Drying                      | $2.8 \times 10^{10}$                  |
| Process Heating                     | $2.4 \times 10^{10}$                  |
| Manufacture of Chemicals (Indirect) | $0.9 \times 10^{10}$                  |
| Operate Pollution Control Equipment | —                                     |

\*Assumed tannery size of 2200 hides/day.

based on a tannery processing 2200 hides per day. Leather drying is the largest savings, with process heat savings also important. Process heating is the heat required to bring aqueous process solutions and rinse solutions up to operating temperatures. In addition, there are some indirect energy savings that relate to the energy requirements for making chemicals used in these operations. As the net consumption of these chemicals is less in solvent processing, there are some energy savings, although of a lower magnitude than the direct heat savings.

These energy savings may be more tangible, as shown in Table IV, where we have an economic basis. The energy dollar savings, and this is direct energy savings only, are shown here. The chemical savings which are derived from more

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TABLE IV  
ECONOMICS OF SOLVENT PROCESSING

| Cost Element                   | \$<br>Savings/Year* |
|--------------------------------|---------------------|
| Energy                         | \$145,000           |
| Chemicals                      | 185,000             |
| Water Supply and Sewer Charges | 144,000             |
| Labor                          | 50,000              |
| FC-113 and MeOH                | —172,000            |
| Depreciation (Increased)       | —35,000             |
| <b>TOTAL</b>                   | <b>\$317,000</b>    |

\*Tannery Size of 2200 Hides/Day.

efficient use of chemical agents are also substantial. There are water and sewer savings because the aqueous steps are avoided completely. The labor requirements are lowered because the hides, once introduced into the equipment, aren't removed until a number of steps later.

However, maintenance of any new equipment will be more demanding and the figure on Table IV is the net change after taking all of this into account. But all of this, of course, has some penalty. There is some consumption of FC-113 and methanol, and there will be some increased depreciation charges because of the new equipment required. The new equipment investment is estimated to be about \$400,000 for a 2200 hide/day tannery with, of course, a rather wide range of uncertainty at this point.

There will be savings in water pollution equipment, both in investment as well as operating costs, but these have not been included because it's not clear what operations will be required. At any rate, on a preliminary cost analysis the economics of solvent processing do look very attractive.

#### SUMMARY

In summary I want to point out that:

There are still many things to be done before we can say the process is fully proved.

At this time we believe FC-113 processing of leather has been established as technically feasible.

There are several leather making operations which can be accomplished in the FC-113 solvent and this saves considerable energy.

There will be reduced water pollution since the solvent is recycled.

The process has generally favorable economics.

All of this has encouraged us to think that, with the increased emphasis at this time on energy conservation and reducing water pollution, the solvent processing of leather may finally be about to fulfill some past expectations.

#### DISCUSSION

MR. MAIRE: Thank you Warren. I think that it is interesting in talking about solvent processing that it is the third year in a row that there has been a paper given on solvent processing at the ALCA meetings. Two years ago, Peter Buechler talked on it; last year I gave a paper on it. This all goes back to the fact that in the late fifties there were three solvent plants in operation in this country. Solvent processing of one type or another has been proven and will work. One question that I have, Warren: you mentioned that the processing time is going to be quite a bit less, so that there would be an inventory savings. What would you estimate the time differential between regular processing and solvent processing to be?

MR. STEINACKER: That is hard to say Max, because we really haven't got far enough in trying to optimize the operations. The effort to date has been more to demonstrate feasibility rather than trying to optimize quality, cost or time. However, based on the solvent work done in the past, it might be one-fifth to one-tenth the conventional time cycles.

MR. MAIRE: Any questions from the floor?

DR. BUECHLER (PPG Industries): I do think that we all have to talk more in terms of solvent processing and savings which can be effected. However, I think that one should not over emphasize the flammability of acetone, because if you are working in closed systems, you are above the 11 percent vapor-in-air mixture which is flammable. You will be above the flammability limit and relatively safe. The drying that I have suggested for acetone recovery in the past has been with nitrogen. On the other hand it would seem that you could get advantages from halogenated solvents, and in fact at Tanners Research Corporation of New Jersey we did try some. We also tried some methanol solvent mixtures. The chief thing is to be able to have a system that is compatible enough to displace the water. The speaker has certainly managed to come up with a

system like that and I want to commend him for it. I do have two questions about his systems of FC-113, nitromethane and methanol. 1) He gives the TLV (threshold limit value for an 8-hour exposure) for a mixture of three materials. In the Material Safety Data Sheets (MSDS) the Department of Commerce is recommending that one use individual TLV's and list them as such. I suppose he calculated it for the mixture. If so it might not be acceptable for use in MSDS until verified by determination of individual components and listed individually. 2) The other thing is that he has some nitromethane present, and I hope he is displacing it, because I believe nitroalkanes as a class of solvents are under extensive investigation by National Institute for Occupational Safety and Health (NIOSH). In the solvent processing and solvent recovery Mr. Steinacker didn't say enough about why nitromethane is there and I would like to know.

MR. STEINACKER: Thank you Peter for bringing up the nitromethane and the fact it concerned you. Prior to this meeting we debated about whether to do away with that particular chart because we no longer use nitromethane. It happened to be in the solvent that we tried first and we had more data using that solvent mixture but now we use only methanol and FC-113.

DR. BUECHLER: How about the TLV's? Were they calculated or determined?

MR. STEINACKER: There is a method in the ACGIH organizations handbook that describes how to calculate the TLV's of mixtures and that is what we did. The particular mixture that we show had only 6 percent methyl alcohol in it. We now believe that we would use a higher concentration of methyl alcohol but without the nitromethane, so I am not sure what the resultant mixture TLV would be. I feel certain that it will be well above the TLV of chlorinated solvents but we haven't really zeroed in on the preferred methanol concentration. That is something that has to be worked on in the future.

DR. BUECHLER: I think that you have answered most of my questions. I just wanted to point out that anybody will have to list the TLV's separately even though one can be calculated for the mixture. The Department of Commerce does not permit that you to use the calculated value and it is so stated in the ACGIH folder. This is fine for your calculations, but you still have to list the individual components.

MR. MAIRE: Any other questions?

MR. EBERLE (Eberle Tanning Co.): Being mainly interested in the bottom line rather than how you do it, I am very curious to know what you can tell us about yields or quality factors from this operation?

MR. STEINACKER: As I mentioned, shrinkage might be a problem. Phil Bartlett, who is here, has been working on this, but hasn't had the time to do much on it. In a couple of scouting attempts Phil has found that the shrinkage can be

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reduced tremendously with some techniques that he has come up with. I am optimistic that it will not be too serious a problem. On the quality aspect we ourselves are not leather experts. We have been working with Steve Fearheller and his coworkers at the Eastern Regional Research Center, U. S. Department of Agriculture in Philadelphia. They have helped us look at some of the leather. They indicate the leather is good enough that the process is worth looking at a little more. So far we have only tried to demonstrate the feasibility of the process but eventually we will have to put our efforts on optimizing other factors and I am sure we will be able to do better than these first attempts.

Mr. MAIRE? Any more questions:

Mr. HOPKINS (ERRC, USDA): Just one question. Did you say you used a closed system for the operation?

Mr. STEINACKER: Yes. A closed system is an absolute requirement, because the boiling point of the solvent is relatively low and the losses of solvent vapor could make it uneconomical. The emphasis is going to be to keep solvent in containment equipment and cut solvent losses as much as possible.

Mr. HOPKINS: That was in a hide processor, right?

Mr. STEINACKER: Yes.

Mr. HOPKINS: It is very interesting because, we have a process for preservation that we feel needs to be used in a system like this and I would like to discuss this with you later.

Mr. MAIRE: Any other questions from the floor? If not thank you again, Warren for a good paper. The next paper is on "The Potential for Process Heat Applications of Solar Thermal Systems in a Tannery" and will be presented by Mr. Chris Harmer, Intertechnology Corporation.

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